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The question of reliability was addressed in this paper by pointing out that control of ozone disinfection can easily be accomplished by monitoring just one parameter, the exhaust gas ozone concentration. It was shown in one treatment plant effluent that by maintaining a constant Y_2 of 2.0 mg/L at flow variations of 2 to 1, a target coliform standard of 200 FC/100 ml would be achieved almost 100% of the time, even with moderate fluctuations in ozone demand.

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EFFECTIVENESS OF OZONE AS A MUNICIPAL WASTEWATER DISINFECTANT

by

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BACKGROUND AND HISTORY

Ozone disinfection is a proven technology. It has been demonstrated repeatedly to be an effective method of achieving bacteriological discharge standards[1,2,3]. According to to the recently completed 1982 Needs Survey conducted by the U.S. Environmental Protection Agency (computer tape, unpublished), there are a total of 32,495 wastewater treatment plants in the United States in various stages of planning, design, operation, or construction. Of those, 15,514 disinfect with chlorine, 441 dechlorinate, 54 ozonate, and 53 use other disinfection methods. At the time of this writing, attempts were being made to access the tape to obtain a clearer understanding of the current status and locations of the various treatment plants mentioned. This task has not yet been completed, but the information will be incorporated into EPA's Process Design Manual for Wastewater Disinfection, scheduled for publication in late 1984. Nevertheless, decisions clearly have been made to build ozone disinfection facilities in the U.S., and it is the purpose of this paper to review the effectiveness of ozone and to present recently developed views regarding ways to improve its effectiveness, cost, and reliability.

Factors influencing disinfection effectiveness

No review would be complete without re-examining the important differences between applied and absorbed ozone dose[4]. The applied dose is the concentration of ozone in the feed carrier gas multiplied by the gas-to-liquid flow ratio. Mathematically, the relationship is given as follows:

$$D = Y_1 Q_G / Q_L \qquad (1)$$

where D = applied dose, mg/L_{liq}

Y_1 = ozone concentration in carrier gas, mg/L_{gas}

Q_G = gas flow rate, L_{gas}/min

Q_L = liquid flow rate, L_{liq}/min

When dose is increased by changing the Q_G/Q_L ratio, the transfer efficiency (TE) of the contactor decreases more rapidly than when dose is increased by changing the Y_1.

The absorbed ozone dose is the difference between the ozone concentration in the inlet and exhaust gas streams multiplied by the Q_G/Q_L ratio:

$$T = (Y_1 - Y_2)Q_G/Q_L \qquad (2)$$

where T = absorbed ozone dose, mg/L_{liq}

Actually, equation (2) merely describes that amount of ozone that has been transferred from the gaseous phase to the liquid phase and does not account for the amount of ozone that has been consumed in chemical reactions. Thus, technically, T is not the absorbed dose but rather the transferred dose, for it consists of both consumed ozone and unconsumed residual. Consequently, for the remainder of this paper, I will refer to T as the amount of ozone transferred to solution.

The importance of T on disinfection efficiency cannot be overstated. Its level is unique to a given effluent quality, contactor design, and degree of reduction in coliform number. Gan et al.[6] reported residual dissolved chemical oxygen demand (COD) and nitrite had the greatest influence on disinfection with ozone, while suspended solids had little effect. Venosa et al.[4] confirmed this observation when they compared filtered and unfiltered secondary effluent. Improved disinfection in filtered effluent was attributed more to removal of COD than of suspended solids. Given and Smith[3] developed a model predicting effluent indicator levels as a function of T and biochemical oxygen demand (BOD). Other workers[2,7] reported similar findings. More recently, Venosa and Meckes[8] found that manganese consumed some of the transferred ozone in a certain secondary effluent and this resulted in higher coliform numbers. Clearly, both organic and inorganic demand play a crucial role in influencing the amount of ozone required to disinfect a given effluent to a particular coliform density. Later in this paper, I will show how this knowledge can be put to practice in improving the reliability of the process.

OPERATIONAL EXPERIENCE

In 1982, EPA contracted with the engineering firm of Roy F. Weston, Inc., to survey existing ozone facilities and determine, analyze, and prioritize operation and maintenance (O&M) factors affecting operational efficiencies of those facilities. Seven municipal wastewater treatment plants and five municipal water treatment plants were visited and the operating personnel interviewed. A listing of the plants visited is presented in Table I.

TABLE I. List of ozone plants surveyed.

No.	Plant	Location
1	Rocky River Regional WWTP	Concord, NC
2	Upper Thompson San. District WWTP	Estes Park, CO

TABLE I. List of ozone plants surveyed. (cont'd)

No.	Plant*	Location
3	Frankfort WWTP	Frankfort, KY
4	Southwest WWTP	Springfield, MO
5	Brookings WWTP	Brookings, SD
6	Murfreesboro WWTP	Murfreesboro, TN
7	Madisonville WWTP	Madisonville, KY
8	Monroe WTP	Monroe, MI
9	Bay Metro WTP	Bay City, MI
10	Charles J. des Baillets WTP	City of LaSalle, CAN
11	Pierrefonds WTP	City of Pierrefonds, CAN
12	Sherbrooke WFP	Sherbrooke, CAN

*WWTP ... Wastewater Treatment Plant
WTP ... Water Treatment Plant
WFP ... Water Filtration Plant

Information was compiled in the form of individual plant trip reports and a draft final report prepared. At the time of this writing, the final manuscript was still being edited.

Time and space limitations preclude a detailed description of the Weston findings. Only those salient features pertinent to this paper will be summarized.

With respect to system control, 6 of the 12 plants adjusted dose manually in response to changes in flow rate. Four provided automatic flow proportional control and one controlled dose automatically by monitoring dissolved ozone residual with an amperometric analyzer. One treatment plant was inoperative during the survey but was designed to provide automatic flow proportional control.

A summary of most of the problems encountered at the ozone plants is given in Tables II and III.

TABLE II. O&M problems reported by plant operators.

- Severe foam problems with contact tank gas recovery system, due to reaction between gas supply and surfactants.
- Ozone system electronics too complicated for WWTP personnel to perform routine maintenance and repair work.
- Too many pieces of equipment that must be maintained.
- System instrumentation must be continually calibrated.
- Ozone generators are a high maintenance item, continually blow fuses.

TABLE II. O&M problems reported by plant operators. (cont'd)

- Improper (i.e., too high) dew point setting causes dielectric failures.
- Excessive heat build-up in O_3 generator room causes generator heaters to shut down units.
- A full-time instrumentation person needed to monitor and maintain O_3 system.
- Improper cleaning procedures for dielectric tubes causes pitting and cracking of tubes.

Table III. Equipment problems reported by plant operators.

- Numerous ozone generator failures.
- Silicone control rectifier (SCR) failures, causing system shutdown due to power surges.
- Corrosion problems with O_3 analyzer valve components, causing frequent cleaning and recalibration.
- Ozone contact tanks constructed below the system control room and O_3 leaks cause instrumentation rubber seals to corrode.
- System equipment (i.e., generators, compressors) very noisy.
- Corrosion problems with compressors due to wet gases.
- Catalyst poisoning in O_3 destruction system.
- Dew point indicators not reliable or not provided.
- Non-compatible materials of construction; rubber sleeves on compressors; chlorinated rubber-based paint used to seal ozone contact chamber.
- Ozone meters unreliable.

The most frequent or prevalent problems encountered were:

- inefficient ozone destruction in destruct unit.
- ozone generator cell failure.
- ozone leakage from generator.
- inefficient performance of inlet air desiccant dryer.
- ozone contactor improperly sealed.
- malfunctions in ozone monitors.

Remedial actions recommended in the report are too numerous and specific to delineate here. It is evident from studying the nature of the problems, however, that most are related to equipment deficiencies and can be remedied by proper equipment selection. This caution should be exercised both by the consulting/design engineer and the equipment manufacturer. The O&M picture presented above readily points out a major reason why a process design manual for wastewater disinfection is so urgently needed.

CONTROL OF DISINFECTION EFFECTIVENESS

In a previous investigation, Venosa and Meckes[8] discussed pilot plant data from six different treatment plant effluents indicating an excellent non-linear correlation between the concentration of ozone in the exhaust gas from the contactor and the total and fecal coliform levels in the final effluent. Exhaust gas monitoring as an operational control strategy to achieve disinfection was suggested to have the following advantages: (1) true ozone is being measured, not total oxidant, as would be the case if dissolved residual were being measured by standard method; (2) the reaction is instantaneous and simple to conduct; (3) it is easily automated; (4) it is useful on a wide variety of secondary effluents; (5) it is not subject to interferences; and (6) it is not adversely affected by sudden shifts in effluent quality. The authors placed one restriction on use of the strategy: the gas to liquid flow ratio must remain constant, since transfer efficiency changes with the Q_G/Q_L ratio. The control approach was then envisioned as follows: gas flow would be paced to liquid flow by a flow proportional signal while monitored exhaust gas ozone levels would automatically signal changes in the power to the generator to compensate for the altered exhaust gas concentration. The above hypothesis was recently subjected to rigorous testing in a pilot field test described in the following sections.

Process Control Theory

The above control strategy can be further simplified if one makes the assumption that, as long as the Q_G/Q_L ratio is less than 0.5, small changes in the ratio do not substantially affect the contactor transfer efficiency (TE). In other words, it is not unreasonable to accept small changes in TE if the operator is permitted the advantage of not having to control his gas flow proportional to his liquid flow while at the same time controlling his ozone concentration. Thus, the gas flow can be held constant and the liquid flow allowed to vary naturally.

With this in mind, we can rearrange equation (2) and solve for Y_2:

$$Y_2 = Y_1 - TQ_L/Q_G \qquad (3)$$

By inspection, it becomes evident that, at a constant Q_G, if Q_L doubles, Y_2 decreases. This results in a signal being transmitted to the ozone generator to increase Y_1, thereby compensating for the increase in Q_L and corresponding decrease in Y_2. Y_2 returns to

normal and the amount of ozone transferred (T) remains relatively unchanged.

It is also evident from equation (3) that, if a sudden increase in demand takes place in the effluent, due, say, to an unexpected organic overload to the plant, T will increase, causing a corresponding decrease in Y_2. Again, a signal will be transmitted to the ozone generator to compensate by increasing Y_1 until the demand has been satisfied. Y_2 will then return to normal. Clearly, a simple means of controlling ozone disinfection is possible by merely monitoring one parameter, the exhaust gas ozone concentration.

Experimental Approach

An experimental ozone pilot plant, used in previous investigations and described elsewhere[4,5,8], was set up at a local conventional activated sludge plant, the Fairfield Wastewater Treatment Plant, located north of Cincinnati. A small side stream of unfiltered, unchlorinated secondary effluent was pumped to the ozone contactor continuously at varying flow rates. To simulate diurnal flow variation at the plant, the peak flow of 130 L/min was always set in the the late morning, a lower flow of 100 L/min in the early afternoon, and the lowest flow of 70 L/min in the late afternoon. Thus, in contrast to previous studies in which conditions were randomized within a run day, conditions in this experiment were fixed to correspond approximately to an actual treatment situation.

Oxygen flow to the contactor was always held at a constant 35 L/min. Thus, the three Q_G/Q_L ratios were 0.27, 0.35, and 0.50.

In order to determine the Y_2 needed to achieve a constant fecal coliform density of 200/100 mL, a dose-response curve was generated. Applied dose levels ranging from 4.6 to 13.0 mg/L at various Q_L and Q_G rates were administered and replicated over a three-day period. Results were plotted on log-log paper to linearize the data (Figure 1). The dasned line signifies the target fecal coliform density of 200/100 mL. From the regression line, the exhaust gas ozone concentration needed to achieve the target fecal coliform level was 1.2 mg/L. If the latter had been used as the control set point, however, the standard would only have been achieved with 50% confidence because of the scatter in the data. In order to comply, say, with 80% confidence ($1-\alpha = 0.8$), the following equation was used to compute the needed exhaust gas level:

$$y = \bar{y} + m(x-\bar{x})^2 + s_e t_{(1-\alpha)} [1+1/n + (x-\bar{x})^2/\Sigma_x]^{0.5} \quad (4)$$

where $$\Sigma_x = \sum_{i=1}^{n} (x_i-\bar{x})^2 \quad (5)$$

y = $\log_{10}$ target fecal coliform standard

$\bar{y}$ = overall mean $\log_{10}$ fecal coliform level

x = $\log_{10}$ exhaust gas ozone needed to achieve y

$\bar{x}$ = overall mean $\log_{10}$ exhaust gas ozone

m = slope of regression line

S_e = standard error of the estimate

$t_{(1-\alpha)}$ = t-statistic at the $1-\alpha$ significance level

n = number of data points

The exhaust gas ozone concentration needed to achieve the target fecal coliform standard with 80% confidence was computed from equation (4) to be 2.0 mg/L. This was used as the set point for subsequent field testing.

Analytical Methods

Ozone concentrations in both the feed gas and the exhaust gas were monitored continuously by ultraviolet photometers (Dasibi analyzers). In addition, the accuracy of the Dasibi readings was checked by analyzing grab samples of gas by the iodometric wet chemistry method[4,9]. The latter measurements were always done at the same time grab samples for bacteriological analysis were collected. Fecal coliforms were enumerated by the standard membrane filtration procedure[10].

Results

Experiments were conducted on 15 independent run days. On each day, 3 separate Q_L's were run, as stated above. All samples were taken in duplicate.

Figure 2 summarizes the day to day variations in the applied dose needed to achieve the constant 2.0 mg/L exhaust gas ozone concentrations. The doses ranged from 5.8 to 9.9 mg/L, reflecting expected daily differences in effluent quality and thus ozone demand. Figure 3 summarizes the fecal coliform data. The three duplicated daily grab samples were averaged for each of the 15 run days. On this basis, compliance with the target fecal coliform level was 100%. This is somewhat misleading, however, for the data as presented do not account for the within-day variation in fecal coliform levels after ozonation at the three different flow rates. Figure 4 presents the latter information. Clearly, the higher the liquid flow rate, the higher the fecal coliform numbers after ozonation. Nevertheless, compliance was still nearly 100%, with only one data point falling above the target line.

In an attempt to explain the between-day variation in applied dose needed to achieve a constant off-gas level, linear regression analyses were performed on the data. No correlation was found between dose and total chemical oxygen demand. A significant correlation was found, however, between dose and the concentration of nitrite in the effluent entering the contactor (Figure 5). For every 1.0 mg/L nitrite present in the effluent, 1.9 mg/L more ozone was transferred from the gas to the liquid. Moreover, analyses of the effluent after ozonation revealed that nitrite had been completely oxidized by the ozone. Thus, if a plant is nitrifying, the degree to which nitrification is achieved will directly influence the effectiveness of ozone disinfection.

The foregoing data presentation has provided direct evidence supporting the process control theory mentioned earlier. As Q_L increased, the Y_1 had to be increased to maintain a constant Y_2. Similarly, at a constant Q_L, as T increased (due to higher levels of nitrite), the Y_1 had to be raised to meet the additional demand. In neither instance was the ability to meet the target fecal coliform standard compromised.

MEETING STRICTER STANDARDS

When the Environmental Protection Agency deleted the fecal coliform standard from the definition of secondary treatment[11], the individual states set their own standards based on the water quality criteria of their respective receiving streams. For those areas where strict standards are enforced, the effectiveness and reliability of disinfection processes are of major importance.

Recently, we decided to investigate the combination of two conventional disinfection processes, ultraviolet light and ozone, to achieve the shellfish standard of 14 fecal coliforms/100 mL in secondary effluent. Details of the study appear elsewhere [12]. Only highlights will be addressed here. A three-column bubble diffuser ozone contactor was modified by incorporating in the middle column a makeshift assembly housing 14 ultraviolet lamps. This enabled us to evaluate UV light after ozone, before ozone, and with ozone in the same column. The effect of UV light and ozone alone were used as controls. Data from a typical experiment are summarized in Figure 6. The ozone dose required to achieve the 14 FC/100 ml target was reduced by UV light from 14 mg/L to 2.8 mg/L, an 80% reduction. This was achieved either with UV light preceding or following ozone. Simultaneous application of the two disinfectants was significantly inferior, due to interference of UV transmission caused by bubbles of ozonized gas in the reactor and to direct absorption of UV light by ozone.

An economic analysis was conducted to determine the conditions under which implementation of both technologies would be justifiable on the basis of cost. Space limitations preclude a detailed discussion here. Figures 7, 8, and 9 summarize results of the analysis as a function of plant size. Clearly, combining UV light

and ozone in a sequential arrangement was found to be more cost-effective than either ozone or UV light alone for plant sizes greater than 38,000 m^3/d (10.0 mgd). For plant sizes less than that, UV appears to be more economical.

SUMMARY

This paper reviewed factors influencing the effectiveness of ozone as a wastewater effluent disinfectant. In a brief selected review of the literature, it was shown that demand of the effluent plays an important and sometimes not so easily predicted role in defining the dose requirement to achieve a given fecal coliform criterion. Important factors include BOD, COD, and nitrite, while less important are suspended solids.

The current O&M outlook, as depicted by the as yet unpublished report of Roy F. Weston, indicates an apparently effective technology that has been hurt by design inadequacies and equipment inefficiencies both on the part of the equipment suppliers and design engineers. EPA's upcoming process design manual on wastewater disinfection should go a long way in laying to rest these shortcomings.

The question of reliability was addressed in this paper by pointing out that control of ozone disinfection can easily be accomplished by monitoring just one parameter, the exhaust gas ozone concentration. It was shown in one treatment plant effluent that, by maintaining a constant Y_2 of 2.0 mg/L at flow variations of 2 to 1, a target coliform standard of 200 FC/100 ml would be achieved almost 100% of the time, even with moderate fluctuations in ozone demand.

Finally, if stricter standards are required to be enforced, combining ozone with ultraviolet light in sequence is economically more effective than either UV light or ozone alone for treatment plants greater than 38,000 m^3/d (10.0 mgd).

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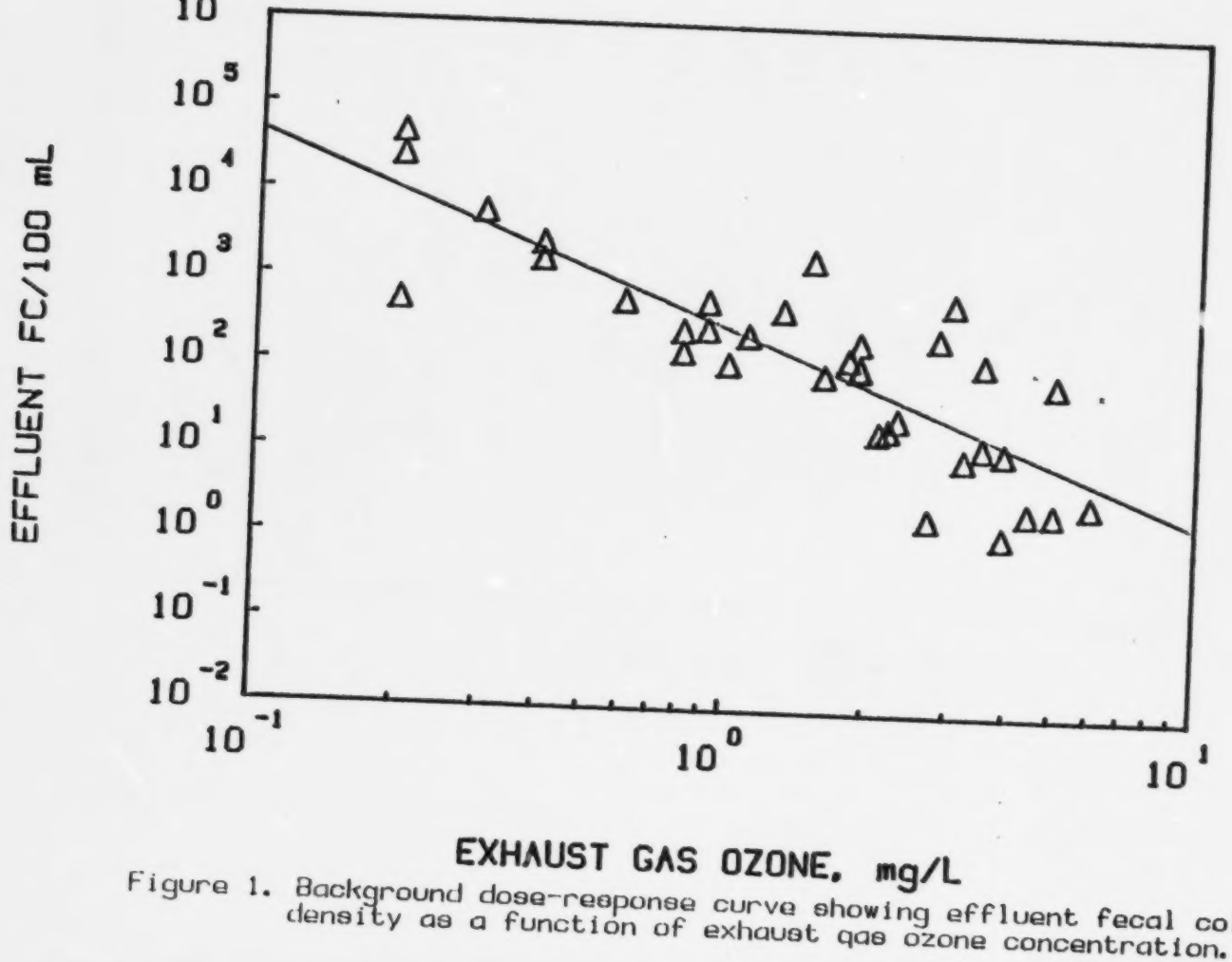

Figure 1. Background dose-response curve showing effluent fecal coliform density as a function of exhaust gas ozone concentration.

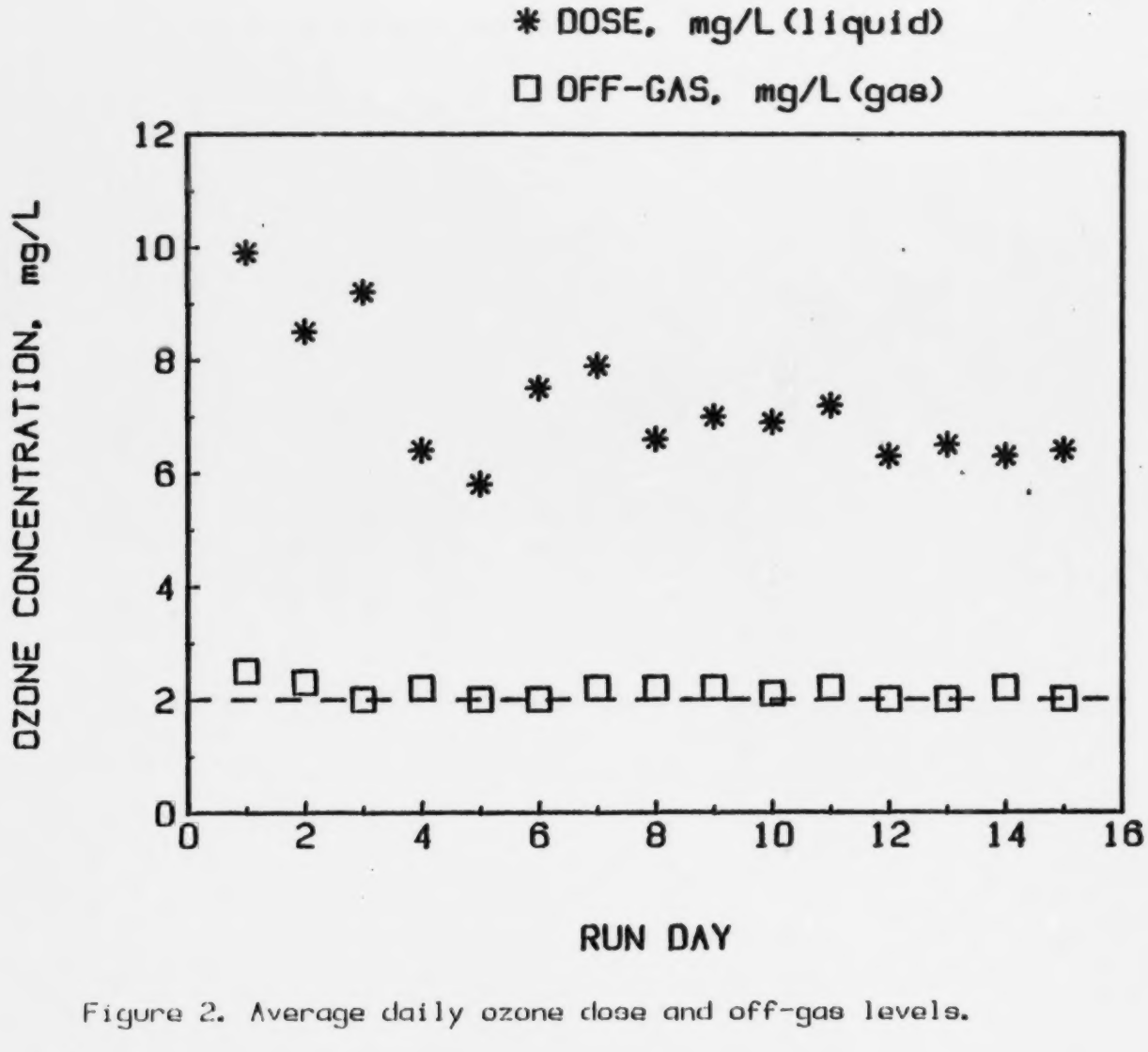

Figure 2. Average daily ozone dose and off-gas levels.

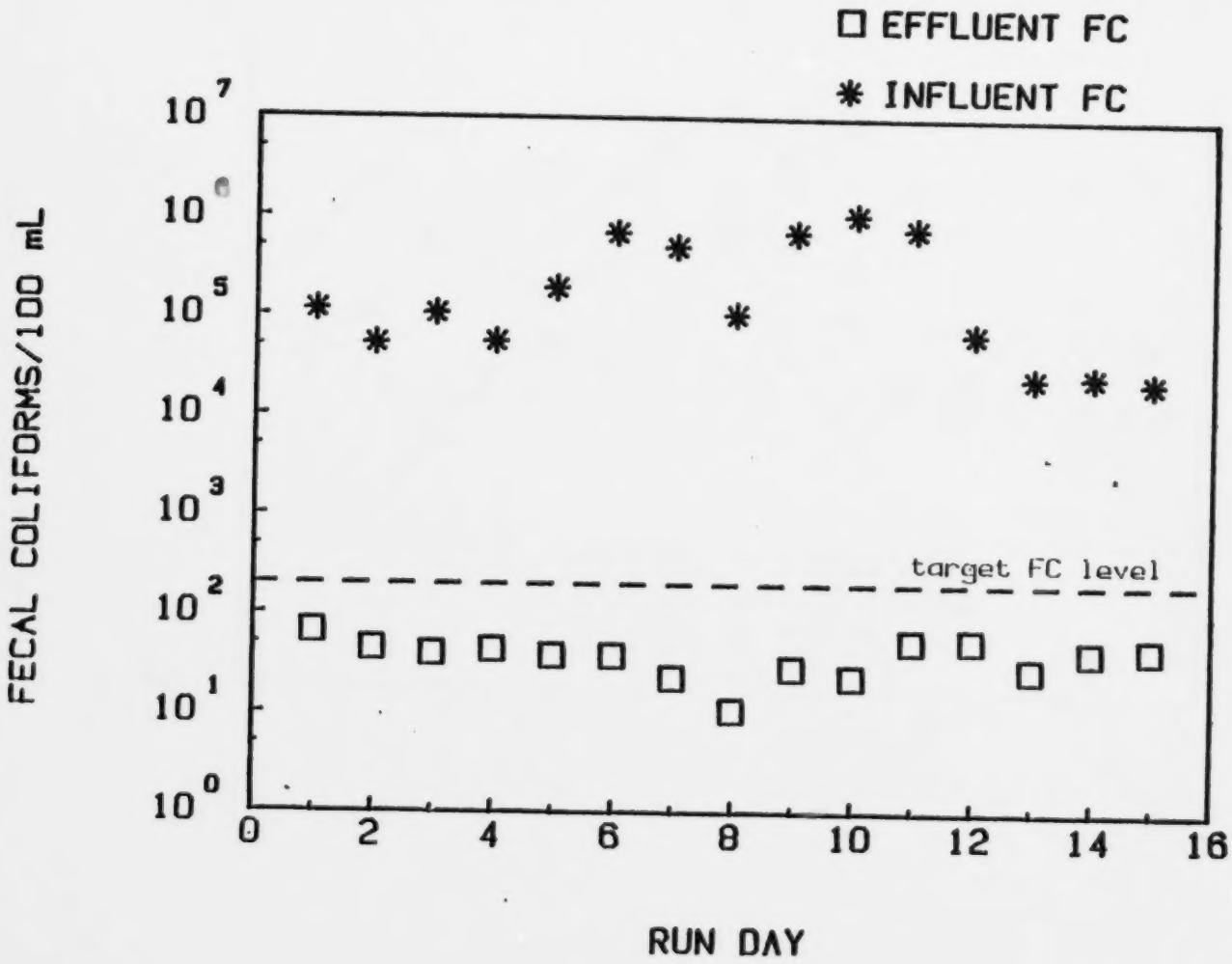

Figure 3. Average daily fecal coliform levels before and after ozone.

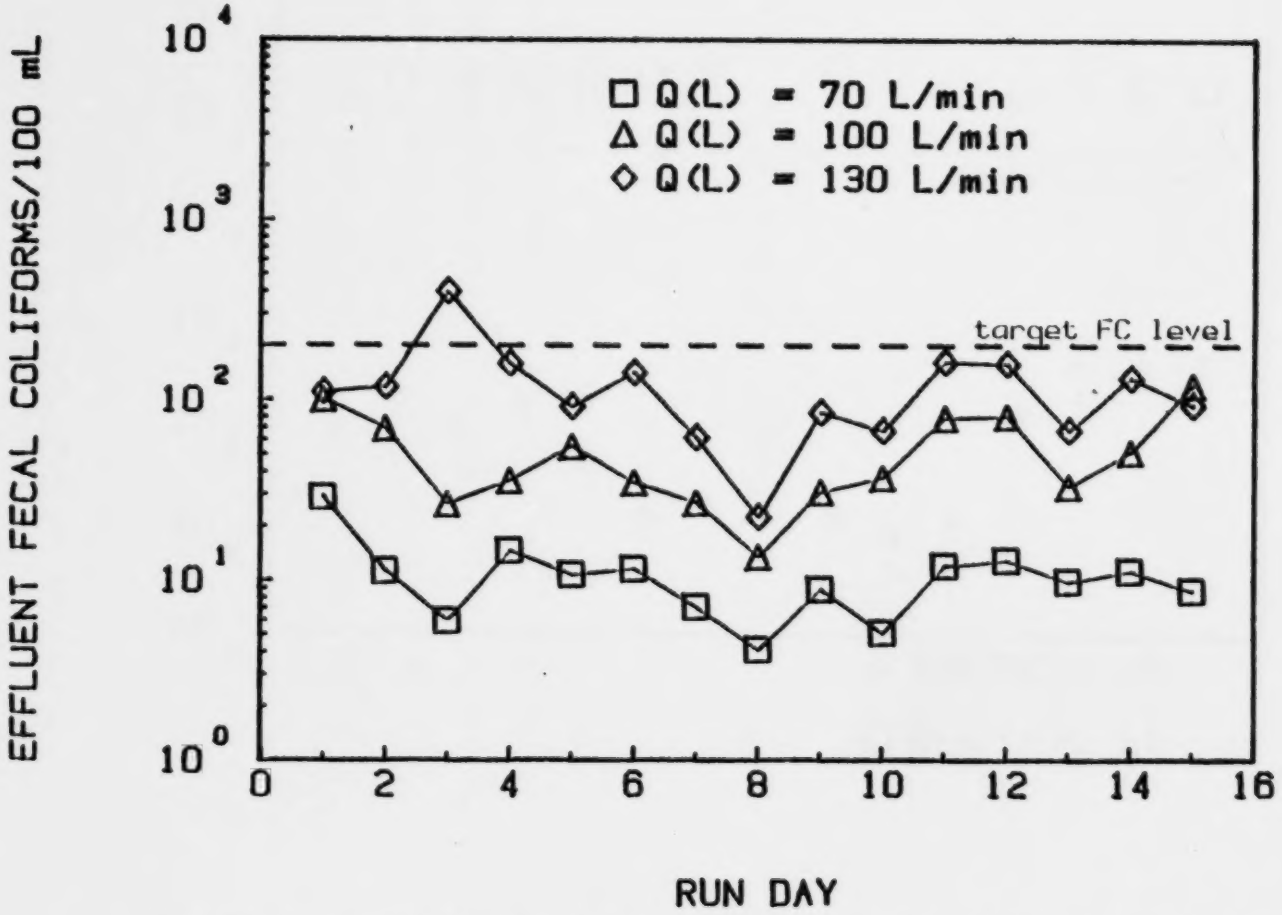

Figure 4. Average daily fecal coliform levels after ozone at each of the three liquid flow rates.

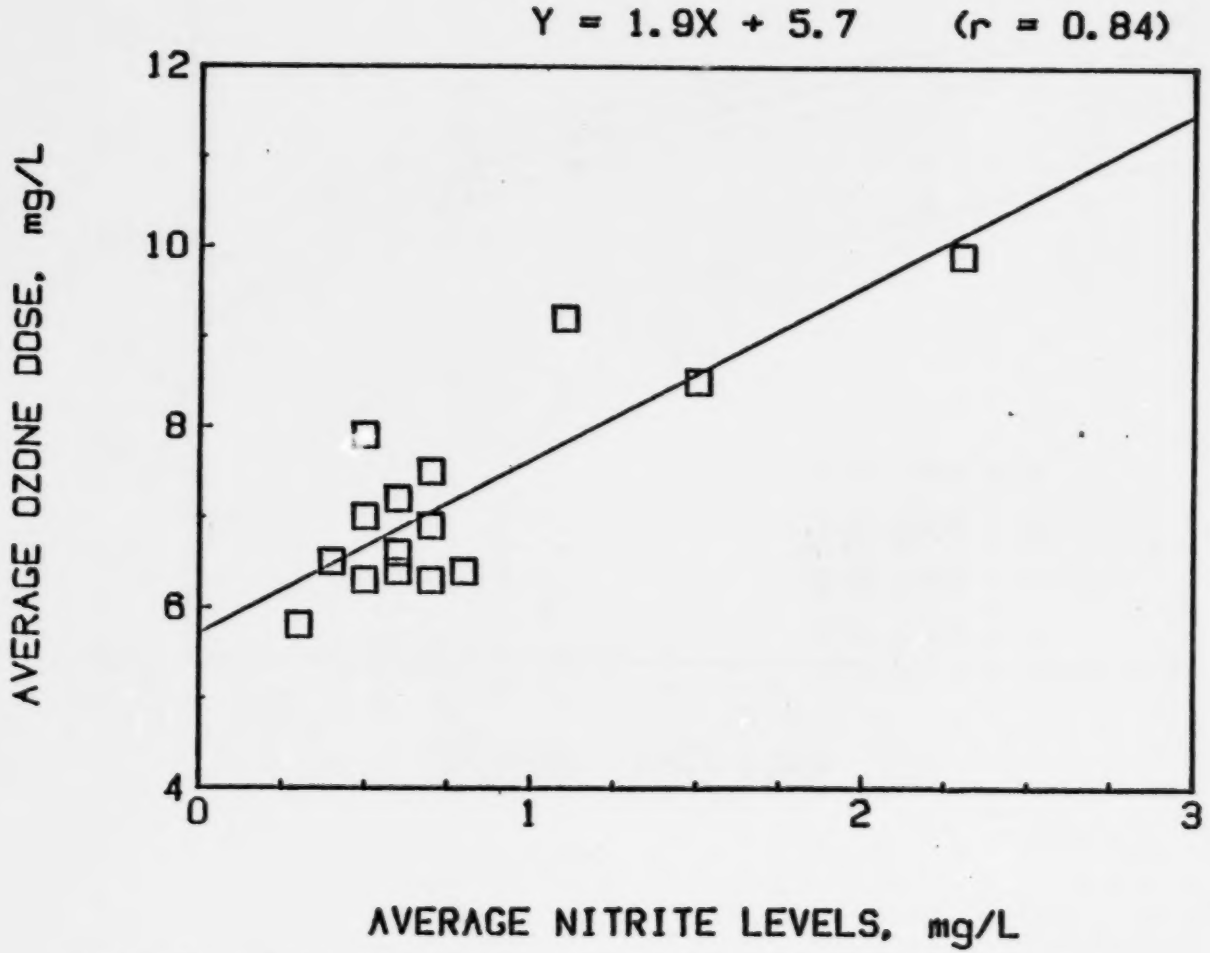

Figure 5. Effect of nitrite on the ozone dose needed to achieve a constant off-gas level of 2.0 mg/L.

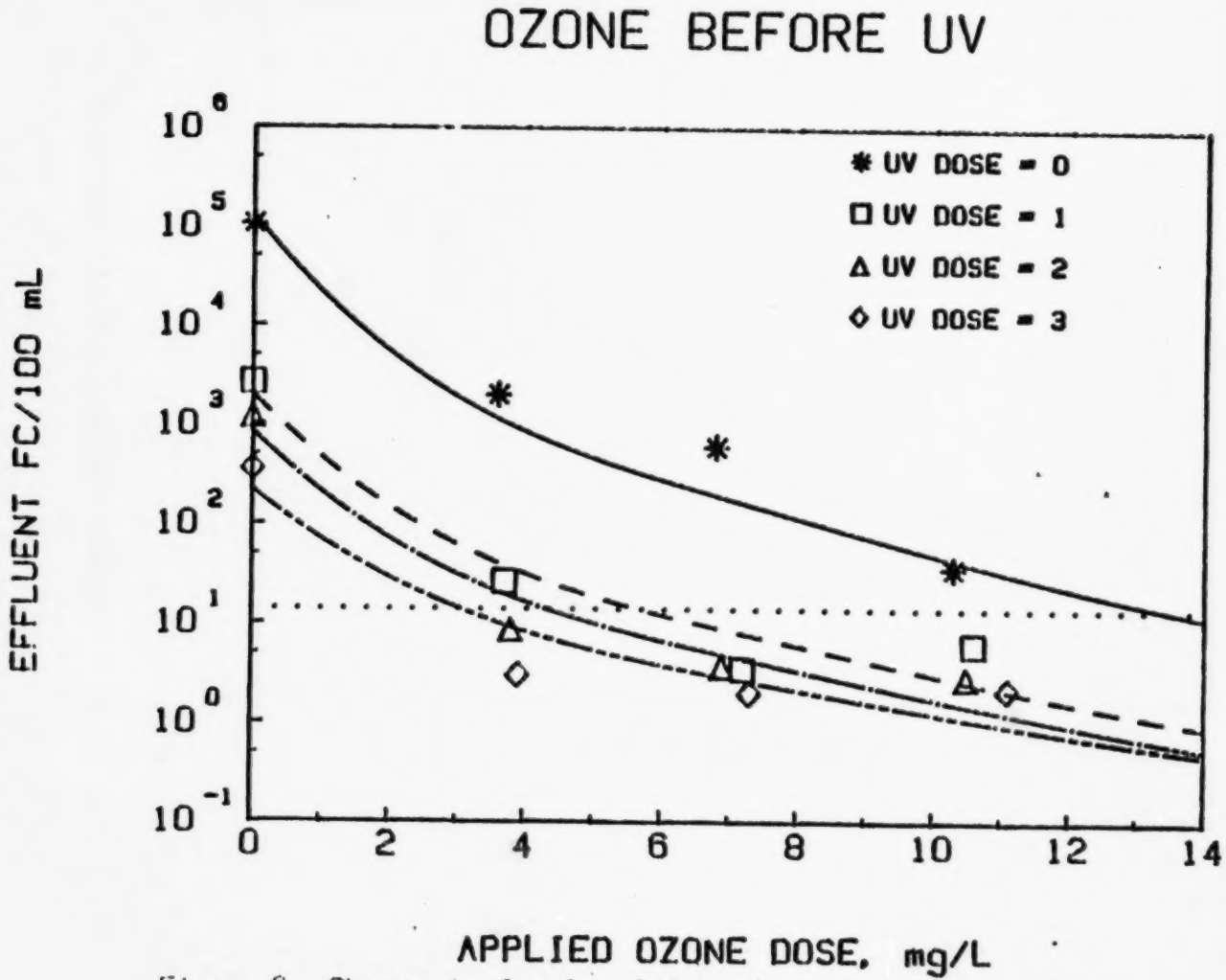

Figure 6. Change in fecal coliform levels as a function of applied ozone dose at various UV doses (condition 1).

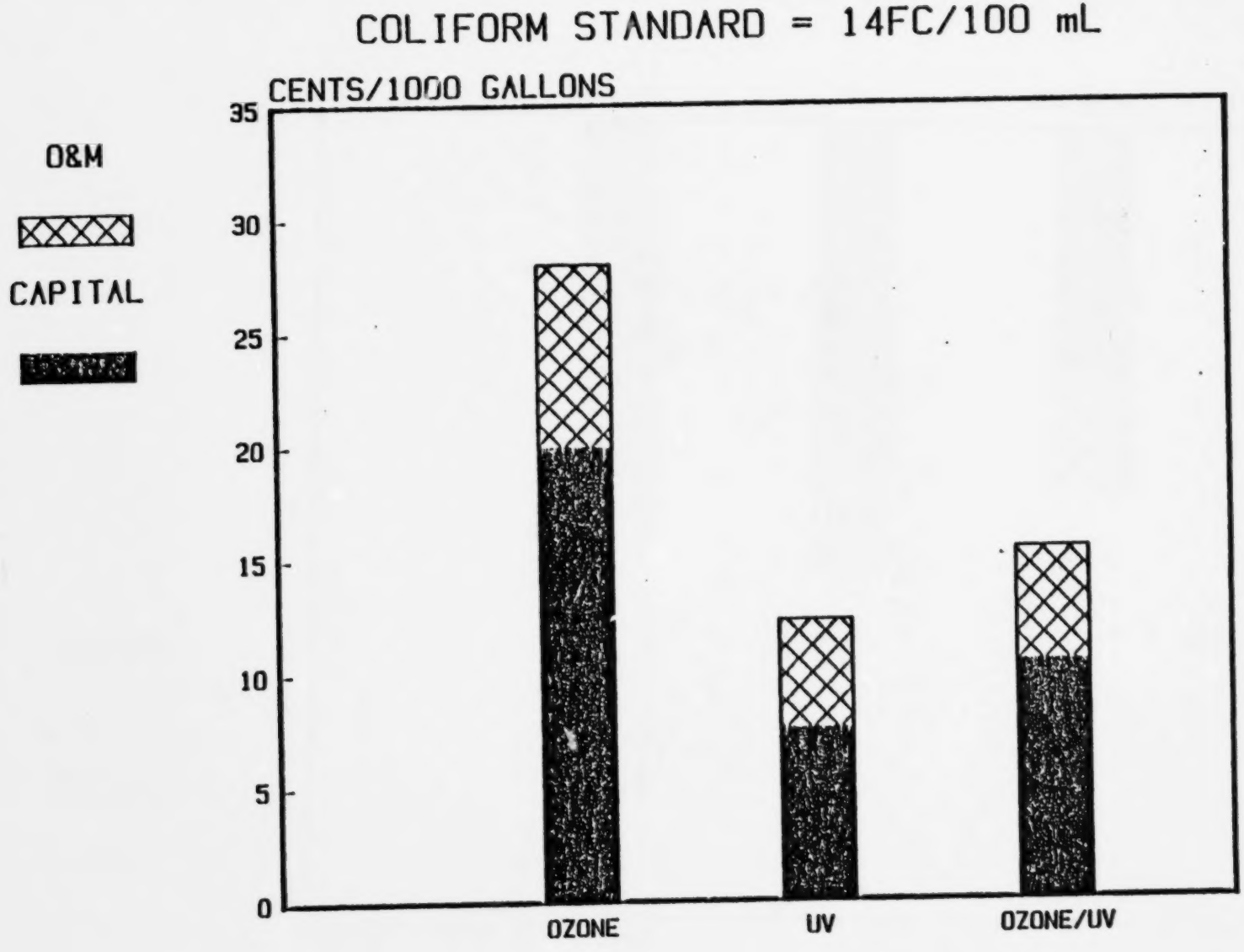

Figure 7. Summary of unit costs at a plant flow of 1.0 mgd (1.0 mgd = 3800 cubic meters/day).

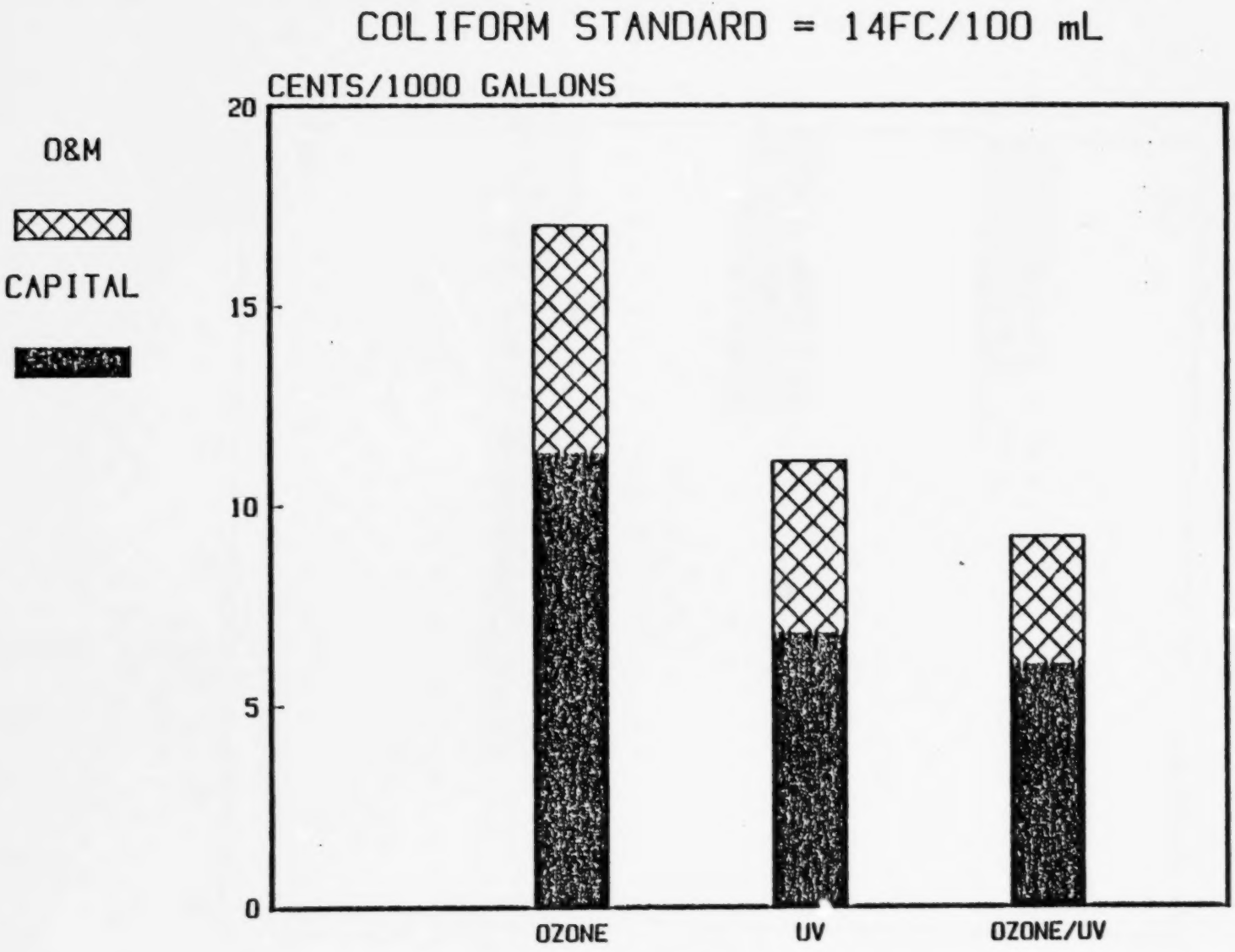

Figure 8. Summary of unit costs at a plant flow of 10.0 mgd (10.0 mgd = 38,000 cubic meters/day).

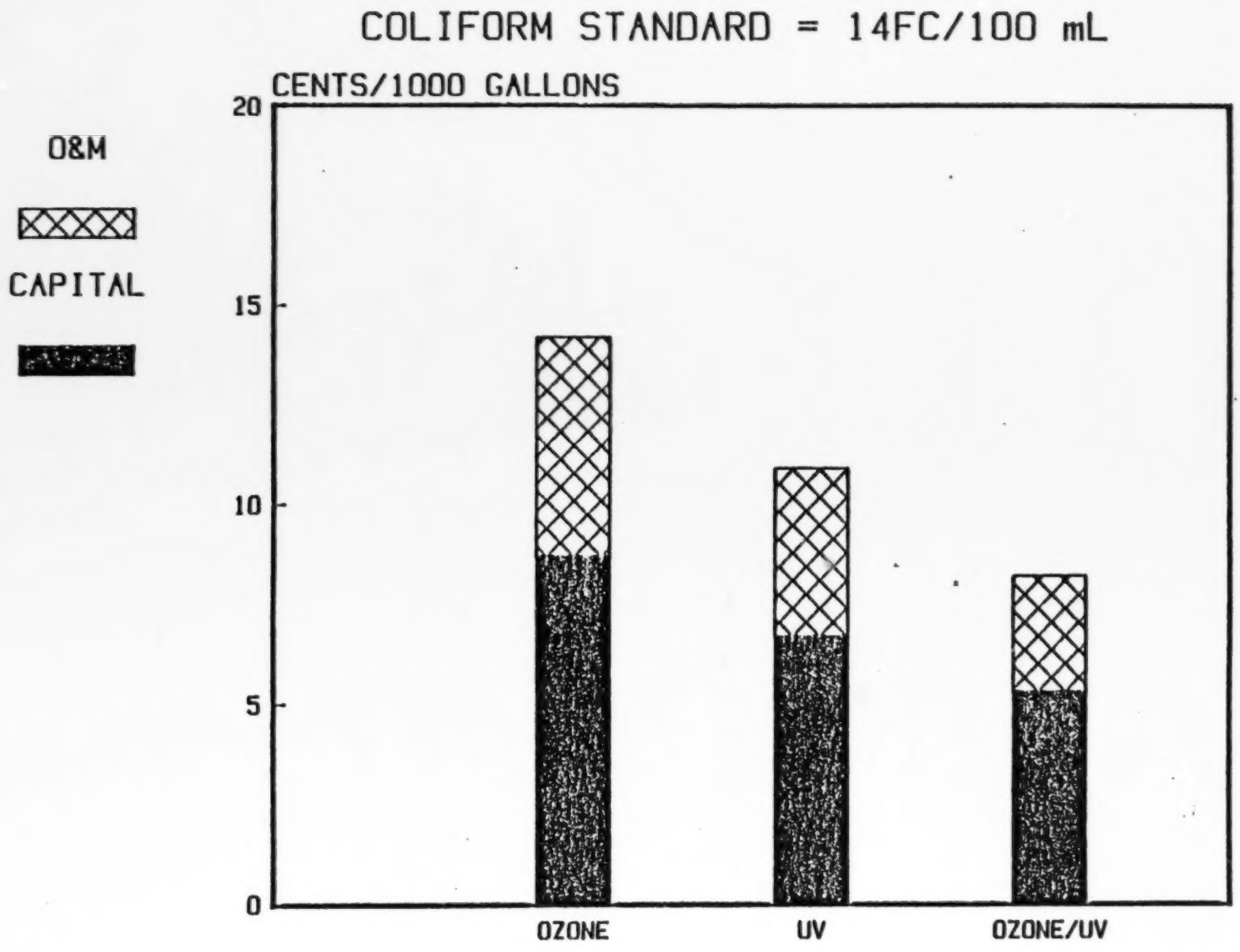

Figure 9. Summary of unit costs at a plant flow of 25.0 mgd (25.0 mgd = 95,000 cubic meters/day).